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Substituent Effect on Corrosion Inhibition of Schiff Bases Derived from Isatin

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ABSTRACT

Two Schiff bases, 3-(4-hydroxyphenylimino)-1,3-dihydroindol-2-one (OPI) and 3-(4-Chloro-phenylimino)-1,3-dihydroindol-2-one (CPI) were successfully synthesized through condensation reactions giving yields of 82% and 63%, respectively. The compounds were characterized via physical and spectroscopic techniques, namely elemental analysis (C, H, N), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and melting point. The corrosion inhibiting property of the Schiff bases on mild steel in 1 M HCl solution was investigated by the weight loss (WL) measurements, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR). The concentrations of the Schiff bases were varied from 1×10^{-3} M to 1×10^{-5} M. The inhibition efficiencies obtained from all the methods employed were in good agreement where the percentage of inhibition efficiencies increased with concentration. OPI showed better inhibition efficiency than CPI with 91% highest inhibition efficiency at 1×10^{-3} M additive concentration. This is likely to be caused by the resonance donating effect due to the presence of the hydroxyl group. The adsorption behaviour obeyed Langmuir isotherm for monolayer formation.

Keywords: *Schiff base, corrosion inhibitors, isatin, mild steel, hydrochloric acid*

INTRODUCTION

The prevention of corrosive attacks in our current metal-based civilization has reached its peak of importance. Acidic medium such as 1 M HCl are often used for various industrial purposes and the combination with mild steel which is susceptible to attack by acids can cause serious metallic corrosion problems [1,2]. Thus, the study of organic corrosion inhibitors has become an attractive field of research to develop novel and efficient corrosion inhibitors [3]. Organic inhibitors generally protect metals from corrosive attacks by forming a protective monolayer film on the metal surface through molecular adsorption. The adsorption may be promoted by the Lewis acid-base interaction caused by the presence of π electrons and electronegative atoms such as nitrogen, oxygen and/or sulphur in the compounds [4]. The relationship between inhibition efficiency and the structure of the molecule are highly important, revolving in the contribution of substituents that can induce a resonance effect or inductive effect [5].

Very few studies on corrosion inhibition of isatin derived compounds on mild steel in hydrochloric acid have been conducted and the literatures were fairly limited [1, 6]. Ahamad *et.al.* (2010) synthesized four isatin derived Schiff bases which showed good inhibition properties at 300 ppm concentration where the most effective inhibitor was reported at 96% [1]. In a recent study by Abdul Ghani *et al.* (2014) two isatin derived Schiff bases, PII and PDI at 1 x 10^{-3} M concentration showed good corrosion inhibition with inhibition efficiencies of 72 and 82%, respectively. Both compounds exhibited adsorption behavior that obeyed the Langmuir isotherm [6].

This paper presents the synthesis and characterization of two Schiff bases, OPI and CPI (Figure 1). The corrosion behaviour of mild steel in 1 M HCl with and without the Schiff bases is also reported through the results of WL, LPR and EIS investigations. Langmuir adsorption isotherms was tested to describe the adsorption behaviour of the compounds. The differences in inhibitive behavior for the two compounds are explained from their structural properties and the substituents effect.

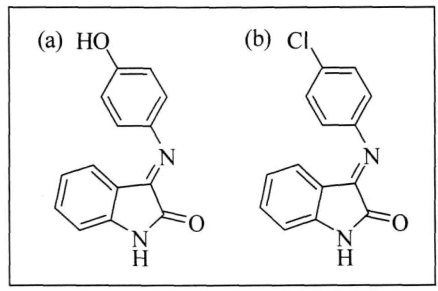


Figure 1: Molecular structure of the investigated compounds, (a) OPI and (b) CPI

EXPERIMENTAL

Synthesis and Characterisation of 3-(4-Hydroxy-phenylimino)-1,3-dihydro-indol-2-one, OPI

A solution of 5 mmol of isatin (0.74 g) in absolute ethanol was added to equimolar solution of 4-aminophenol (0.54 g) in the same solvent. The mixture was refluxed for 6 hours. The red crystals formed were filtered off and washed thoroughly with diethyl ether, and dried under vacuum. Yield = 0.977 g (82%). MP = 288.6°C. Experimental elemental analysis (%): C, 70.09; H, 4.16; N, 11.69. Calculated elemental analysis (%) for $C_{14}H_{10}N_2O$: C, 70.58; H, 4.23; N, 11.76. IR bands (KBr): **ν**C=N = 1611 cm^{-1}; **ν**C=O = 1713 cm^{-1}, **ν**N-H = 3269 cm^{-1}, **ν**C-OH = 2827 cm^{-1}. ^1H NMR (*d*-DMSO, 300 MHz) δ/ppm: 6.67-7.62 (9 H, m, Ar), 10.8 (1 H, s, NH). ^{13}C NMR (*d*-DMSO, 75 MHz) δ/ppm: 111.9-134.5 (CH-Ar), 142.0-147.0 (C-N), 155.8 (C=O), 164.3 (C=N).

Synthesis and Characterisation of 3-(4-Chloro-phenylimino)-1,3-dihydro-indol-2-one, CPI

A mixture of 5 mmol of isatin (0.74 g) and 5 mmol of 4-chloroaniline (0.64 g) was mixed in absolute ethanol and refluxed for 6 hours. The resulting mixture was left overnight to form a yellow precipitate. The product, was then filtered off, washed thoroughly with diethyl ether and dried under vacuum. Yield = 0.806 g (63%). MP = 272.4°C. Experimental elemental analysis (%): C, 65.50; H, 3.44; N, 10.44. Calculated elemental analysis (%) for $C_{14}H_{10}N_2O$: C, 65.51; H, 3.53; N, 10.91. IR bands (KBr): νC=N =

1611 cm^{-1}; νC=O = 1739 cm^{-1}, νN-H = 3264 cm^{-1}, νC-Cl = 1196 cm^{-1}. ^{1}H NMR (*d*-DMSO, 300 MHz) δ/ppm: 6.45-7.52 (8 H, m, Ar), 10.9 (1 H, s, NH). ^{13}C NMR (*d*-DMSO, 75 MHz) δ/ppm: 111.6-134.6 (CH-Ar), 145.5-148.4 (C-N), 154.7 (C=O), 164.4 (C=N).

Weight Loss Measurements

Mild steel coupons (1 cm x 1 cm) were prepared by polishing to a mirror finish using 120, 320, 600, 800 and 1200 grit emery paper, immersed in ethanol, washed with deionized water and dried before being weighed. 50 mL solution of 1 M HCl (as blank) and that containing various concentrations of the Schiff bases were used to immerse the mild steel for 24 hours. The masses before and after immersion were determined using analytical balance for calculation of weight losses. The results were average of triplicates and used to calculate the inhibition efficiencies [7].

Electrochemical Analysis

A conventional three-electrode cell was used for electrochemical measurements. Ag/AgCl electrode with a Luggin capillary and platinum rod served as reference and counter electrode, respectively. The mild steel was embedded in epoxy resin and exposing approximately 0.049 cm^2 of the surface to the test solution. Prior to each measurement, the electrode surface was mechanically abraded with SiC papers up to 1200 grit, degreased by ethanol, rinsed with deionized water and dried. The concentrations of the Schiff bases in 1 M HCl were varied from 1 x 10^{-3} M to 1 x 10^{-5} M. In order to obtain a steady state open circuit potential, the working electrode was immersed into the test solution for 15 minutes before measurements. All experiments were done in triplicates. Electrochemical measurements were carried out using Gamry 600TM potentiostat/ galvanostat connected to a workstation. Electrochemical impedance spectroscopy (EIS) measurements were performed at open circuit potential over frequency range of 0.05 Hz to 100 kHz and the sinusoidal potential perturbation was 10 mV in amplitude with data density of 10 points per decade. Polarization measurements (LPR) were recorded at constant scan rate of 1 mV/s. With potential scan from -0.1 V to 0.1 V which proved sufficient to meet the demand of a Tafel test on mild steel in 1 M HCl. All data were analyzed and fitted using Gamry EChem Analyst software [8].

RESULTS AND DISCUSSION

Weight Loss Measurements

The values of inhibition efficiency and corrosion rate obtained from the weight loss measurements for OPI and CPI at different concentrations are shown in Table 1. The addition of the inhibitors to the corrosive solution of 1 M HCl reduced the dissolution rate of mild steel efficiently. The inhibition of mild steel in the corrosive medium can be attributed to the adsorption of the inhibitors' molecules on metal surface. At the highest concentration of $1x10^{-3}$ M, both OPI and CPI showed good inhibition efficiency of 87% and 74%, respectively. Higher performance of OPI as corrosion inhibitors is likely due to the presence of electron donating group of hydroxyl (OH) in the structure.

Table 1: Inhibition efficiencies for various concentrations of OPI and CPI from weight loss measurements

Schiff Base	Conc. (M)	Weight loss (g)	Inhibition efficiency, η_w (%)	Corrosion rate, R_{corr} (mm/yr)
Blank	-	0.0240	-	11.13
OPI	1×10^{-5}	0.0049	79.6	2.27
	1×10^{-4}	0.0045	81.3	2.08
	1×10^{-3}	0.0031	87.1	1.43
CPI	1×10^{-5}	0.0107	55.4	4.96
	1×10^{-4}	0.0081	66.2	4.03
	1×10^{-3}	0.0062	74.1	2.87

Impedance Measurements

The Nyquist plots of mild steel in 1 M HCl in the presence and absence of OPI and CPI are given in Figure 2 (a) and (b). The impedance parameters are given in Table 2.

The Nyquist diagrams present capacitive loop in the first quadrant indicating that there was only one time constant. Slightly depressed semicircles were observed due to the roughness and inhomogeneities of mild steel surface caused by a phenomenon called dispersing effect [9].

It is apparent that the impedance response of mild steel was significantly changed after the addition of the inhibitors. The diameter of the semicircle increased with the concentrations of both OPI and CPI resulted from the effective surface coverage of the inhibitors on mild steel.

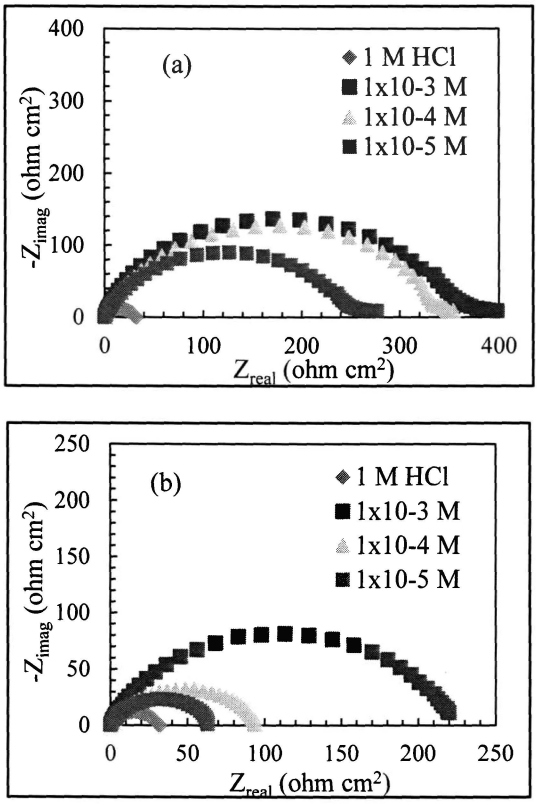


Figure 2: Nyquist plots for mild steel in 1 M HCl in the presence and absence of different concentrations of (a) OPI and (b) CPI

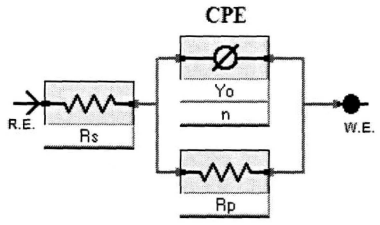
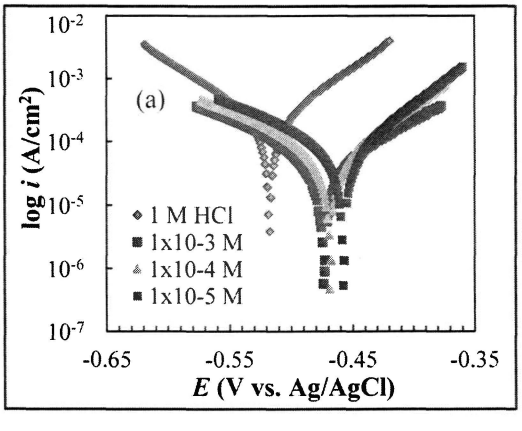


Figure 3: Equivalent circuit fit for the Nyquist plots

Table 2 shows the impedance data acquired from fitting analysis of both inhibitors using the equivalent circuit drawn in Figure 3, where R_s is solution resistance, R_p is polarization resistance and CPE is the constant phase element to replace a double layer capacitance (C_{dl}) for a more accurate fit. The impedance of a constant phase element consists of Y_o which is a proportional factor and exponential parameter and n indicates the degree of surface roughness where small deviation from 1 shows a homogeneous surface. R_p values represent the degree of difficulty for corrosion reaction to occur, where increasing R_p values indicate decreasing corrosion rate [10]. It can be observed from Table 2 that the R_p values increased with inhibitor's concentrations which indicate that corrosion reactions were retarded, thus giving high inhibition efficiency. This effect was more pronounced with OPI, which exhibited higher inhibition efficiency than CPI.

Polarization Measurements

The Tafel plots of mild steel in 1 M HCl at various concentrations of Schiff bases are shown in Figure 4 (a) and (b), whereas the electrochemical parameters are summarized in Table 3.



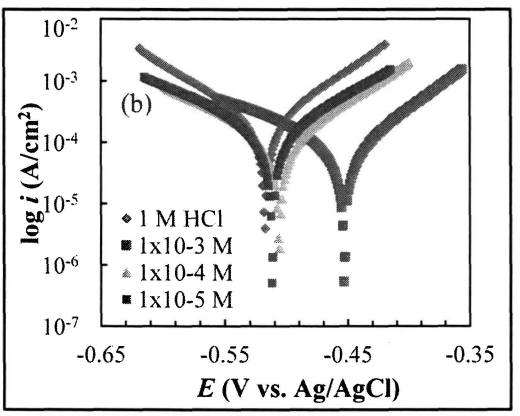


Figure 4: Tafel plots for mild steel in 1 M HCl in the presence and absence of different concentrations of (a) OPI and (b) CPI

The electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes ($ß_a$ and $ß_c$) obtained from the extrapolation of the plots are summarized in Table 3. The addition of OPI and CPI into the corrosive medium of 1 M HCl affects both polarization curves associated with the anodic and cathodic current density, which decreased with increasing concentration of inhibitors. The increase in concentration induced a decrease of anodic and cathodic current densities and produced a small shift in the corrosion potential to more noble values, which indicates that there was growth of a new surface film [11]. Changes in the current density were more prominent in the cathodic domain for OPI making it a cathodic type inhibitor. These results indicate that the hydrogen evolution mechanism was retarded hence reducing the corrosion rate. For CPI, the prominent changes suggest that CPI was an anodic type inhibitor where the dissolution of Fe on the metal surface was retarded. As can be seen from Table 3, the increased concentration of both inhibitors induced a decrease of the corrosion current density, which indicates that the adsorptive film of the inhibitors on the mild steel surface became more stable.

Table 2: Impedance parameters for mild steel electrode in 1 M HCL in the presence of different concentrations of OPI and CPI

	C (M)	R_s (Ω cm^2)	R_p (Ω cm^2)	Y_o (S.sec$^{n/cm2}$)	N	η (%)
Blank	1 M HCl	0.13	31.9	97.2 x 10^{-6}	0.89	-
OPI	1 x 10^{-5} M	0.10	248.2	136.6 x 10^{-6}	0.84	87
	1 x 10^{-4} M	0.14	335.8	124.1 x 10^{-6}	0.82	90
	1 x 10^{-3} M	0.12	362.6	127.8 x 10^{-6}	0.85	**91**
CPI	1 x 10^{-5} M	0.19	65.6	225.7 x 10^{-6}	0.78	51
	1 x 10^{-4} M	0.16	90.1	155.1 x 10^{-6}	0.80	64
	1 x 10^{-3}M	0.12	217.6	166.1 x 10^{-6}	0.82	**85**

Table 3: Polarization parameters for mild steel electrode in 1 M HCL in the presence of different concentrations of OPI and CPI

	C (M)	β_a (mV/ dec)	β_c (mV/ dec)	E_{corr} (mV vs. Ag/AgCl)	i_{corr} (μA/ cm^2)	R_p (Ω cm^2)	η (%)	θ
Blank	1 M HCl	83.0	-91.1	-518.0	235.0	47.9	-	-
OPI	1 x 10^{-5} M	48.1	-62.9	-458.0	46.6	254.0	81	0.73
	1 x 10^{-4} M	71.3	-83.3	-468.0	32.9	301.0	84	0.86
	1 x 10^{-3} M	66.7	-65.1	-473.0	18.1	429.6	**88**	0.92
CPI	1 x 10^{-5} M	47.5	-70.9	-512.0	108.1	128.3	62	0.54
	1 x 10^{-4} M	91.5	-106.5	-506.0	84.5	163.3	70	0.64
	1 x 10^{-3} M	55.5	-70.9	-453.0	61.4	220.1	**78**	0.74

Adsorption Isotherm

Adsorption isotherms are useful to determine the adsorptive behaviour of a corrosion inhibitor as they provide important information on the interaction of the inhibiting compounds with the metal surface. A few adsorption isotherms were tested for the description of adsorption behavior of the studied compounds such as Langmuir, Frumkin and Temkin adsorption isotherm. It was found to obey the Langmuir adsorption isotherm where it explains the passive monolayer formation of the inhibitor onto a mild steel surface through the physisorption and chemisorption phenomenon.

The surface coverage, θ, for various concentrations of the inhibitor was calculated and the plot of C/θ vs. C yields straight lines as shown in Figure 5. Experimental results are in good agreement with Langmuir adsorption isotherm shown in Equation 1 [9]:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (1)$$

where C_{inh} is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant.

The value of K_{ads} is found as 250 x 10^3 and 100 x 10^3 M^{-1} for OPI and CPI, respectively. The increasing value of K_{ads} shows increasing adsorption capability of PDI on metal surface [12] due to its structure. K_{ads} is also related to the standard free energy of adsorption (ΔG_{ads}) according to Equation 2 [9]:

$$K_{ads} = 1/55.5 \exp(-\Delta G_{ads}/RT) \quad (2)$$

where R is the universal gas constant (J mol^{-1} K^{-1}), T the absolute temperature (K) and 55.5 the value for molar concentration of water in solution (mol L^{-1}).

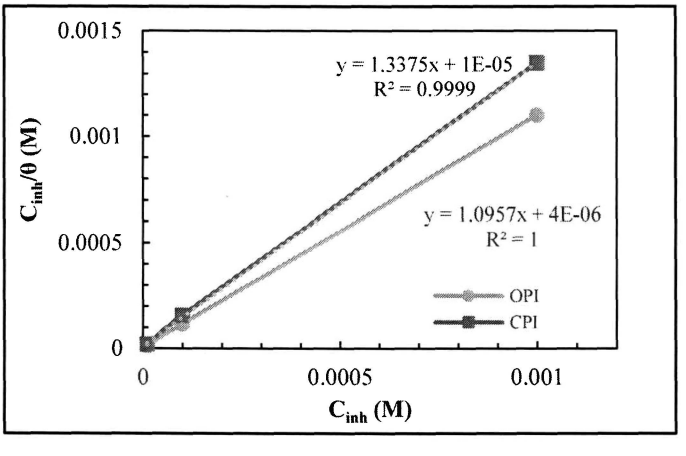


Figure 5: Langmuir plots for OPI and CPI on mild steel in 1 M HCl

Generally, as reported in previous studies [12-15] when the value of ΔG_{ads} is up to -20 kJ/mol, the adsorption is due to physisorption, i.e, electrostatic interactions between charged metal surface and the charged

inhibitor. While for ΔG_{ads} around -40 kJ/mol or higher, the adsorption is chemisorption type, i.e. the formation of coordinate bond between metal surface and inhibitor via charge sharing or electronic transfer [7]. The free adsorption energy values for OPI and CPI are -37.3 kJ/mol and -35.2 kJ/mol, respectively. The calculated ΔG_{ads} showed that the adsorption mechanism of the investigated compounds was physisorption in nature, with a significant contribution of chemisorption mechanism. The more negative value of ΔG_{ads} for OPI indicates that it has a better adsorption capability than CPI with a more spontaneous adsorption of inhibitor molecule on metal surface [15]. The adsorption of these compounds may also be influenced by the presence of substituents that facilitate the adsorption through resonance effects. Compounds containing electron donating groups generally adsorb more efficiently than compounds with electron withdrawing groups due to the enrichment of the aromatic rings. Electron donating groups with a lone pair of electrons such as hydroxyl, OH, can activate the aromatic ring through resonance donating effect where the π electrons are pushed towards the ring and increase the electron density. Therefore, the aromatic ring becomes a better donor with enriched electron density and at the same time enriching the electron density at the azomethine group through inductive effect. Consequently, the inhibition efficiency of the compound increases. Meanwhile, electron withdrawing groups such as chloro, Cl, deactivates the aromatic ring by reducing the electron density through resonance withdrawing effect [16].

CONCLUSION

Both Schiff bases, OPI and CPI were successfully synthesized and characterized. Corrosion inhibition investigations showed that both compounds exhibit excellent inhibitor properties by 91% and 85%, respectively. Higher inhibition efficiency was observed for OPI, likely due to the presence of the hydroxyl moiety, an electron donating group, which enriches the electron density of the aromatic ring and azomethine group of Schiff base. On the other hand, CPI contains an electron withdrawing chloro group making the benzene ring and C=N group electron deficient. Hence, OPI has a higher adsorption strength and form a more stable passive monolayer on mild steel surface to reduce the corrosion rate as it obeys Langmuir adsorption isotherm.

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